

## VERIFICATION OF TRANSLATION

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Sir:

I, Teiko MATSUBARA of c/o Hamamoto & Associates of Bansui  
Building, 5-16, Toranomom 1-chome, Minato-ku, Tokyo, Japan, declare:

(1) that I am well acquainted with both the Japanese and the English  
languages;

(2) that I translated the Japanese Unexamined Patent Publication No.  
6-164004 from Japanese into English; and

(3) that the attached English translation is a true, correct and faithful  
translation to the best of my knowledge and belief.

Dated this 18th day of December, 2001

Teiko Matsubara

Signature by: Teiko MATSUBARA

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(54) Title of the Invention: SUPERCONDUCTIVE DEVICE

(57) [Abstract]

[Object] This invention is aimed to lower the junction barrier between a semiconductor and a superconductor, thereby raising the transmittance of quasiparticles therethrough.

[Construction] This invention provides a superconductive device having a superconductor layer 3 formed over a semiconductor substrate 1 with the intermediary of a metallic layer 2, wherein the metallic layer is made of an alkaline metal, an alkaline earth metal or a lanthanum metal.

[Claimed Scopes for Patent]

[Claim 1] A superconductive device comprising a superconductor layer formed over a semiconductor substrate with the intermediary of a metallic layer, wherein the metallic layer is made of an alkaline metal, an alkaline earth metal or a lanthanum metal.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization]

This invention relates to a superconductive device and in particular to an improvement in the junction between a semiconductor and a superconductor.

[0002]

[Prior Art]

There has been known a superconducting transistor as a device that utilizes a junction between a semiconductor and a superconductor. The present applicant has previously proposed a device that makes use of a junction between an oxide superconductor and a semiconductor for the collector and base junction (as described in detail in Japanese Patent Application No. H3(1991)-224,565).

[0003] According to the method thus proposed, doping a  $\text{SrTiO}_3$  single crystal with Nb in an amount in a range of 0.08 to 0.5 % by weight makes the  $\text{SrTiO}_3$  an n-type semiconductor. And, use is made there of the nature that the Nb doped  $\text{SrTiO}_3$  is of a perovskite structure to cause a film of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (where  $0.2 < x < 0.5$ ) (hereinafter, abbreviated as BKBO) to grow epitaxially. A low energy type superconducting base transistor that utilizes these is shown in Fig. 6. In such a superconducting base transistor, use is made of an oxide semiconductor made up of a  $\text{SrTiO}_3$  single crystal that is doped with Nb in an amount not less than 0.08 % by weight but not greater than 0.5 % by weight to form its collector region 10, and on this collector region 10 is there formed by a sputtering process its base region 11 made of a superconducting film

composed of BKBO. And, on this base region 11 is there formed a dielectric film 12 on which further formed an electrode 13 that is formed, for example, from Au by vapor deposition that serves as the emitter region of the transistor.

[0004]

[Problems to be solved by the Invention]

Forming a superconductor upon a semiconductor produces a barrier ( $\phi_B$ ) between them which is determined according to an intrinsic surface potential provided by the semiconductor (SE) and superconductor (SC) junction (see Phys. Rev. 71 (1947) 717, John Bardeen).

[0005] Fig. 3(a) is a diagram showing energy bands of a semiconductor; Fig. 3(b) is a diagram showing energy bands of a superconductor; and Fig. 3(c) is a diagram showing energy bands of a semiconductor and superconductor junction. In these diagrams, the following denotations apply: V: the vacuum level;  $E_c$ : the bottom of the conductor;  $E_v$ : the top of the valence band;  $E_F$ : Fermi level;  $X_{sc}$ : the work function of the superconductor; and  $2\Delta$ : the superconducting energy gap (with the proviso that  $2\Delta = 0$  at a temperature not less than the superconducting critical temperature  $T_c$ ).

[0006] In general, the barrier  $\phi_B$  is the one to which the difference between the work function ( $X_{SE}$ ) of the semiconductor and the work function ( $X_{SC}$ ) of the superconductor, namely  $X_{SC} - X_{SE}$ , corresponds. This barrier is called the Schottky barrier. As shown in Fig. 3(c), forming the superconductor on the semiconductor makes the barrier  $\phi_B$ , and the asymmetry of the junction gives its current and voltage characteristics a rectifying function. A device that utilizes this rectifying function is called a Schottky diode and is used in a TTL logic or a microwave mixer, or the base and collector junction of a superconducting base transistor. Also in a high energy type superconducting base transistor, this junction is

used as the emitter and base junction (see T. Kobayashi et al, Jpn. Appl. Phys. 25 (1986) P. P. 402).

[0007] By the way, a low energy type superconducting base transistor in which its emitter and base junction is made of a metal, a tunneling layer and a superconductor layer, has quasiparticles which is low energy injected into its superconducting base. This has presented the problem that a high barrier ( $\phi_B$ ) base and collector junction impedes transmittance of quasiparticles into the collector region.

[0008] With the view to overcoming the abovementioned problem met in the prior art, this invention is aimed to lower the barrier at the junction between a semiconductor and a superconductor, thereby raising the transmittance of quasiparticles therethrough.

[0009]

[Means for Solving the Problem]

This invention provides a superconductive device characterized in that it has a superconductor layer formed over a semiconductor substrate with the intermediary of a metallic layer, wherein the metallic layer is made of an alkaline metal, an alkaline earth metal or a lanthanum metal.

[0010]

[Function/Operation]

An alkaline metal, an alkaline earth metal or a lanthanum metal has a work function that is considerably lower than those of ordinary metals. Thus, forming a layer of such a metal in several mono layers (M. L.) or so on a semiconductor makes it possible to lower the work function above the semiconductor. Therefore, forming a junction with superconductor on such a layer of the metal makes it possible to form a barrier ( $\phi_B$ ) that is lowered in height.

[0011]

[Example]

An explanation is given hereinafter in respect of

example of this invention with reference to the drawing figures.

[0012] The work functions of an alkaline metal, an alkaline earth metal and a lanthanum metal are, for example, 2.14 eV for Cs, 2.87 eV for Ca, and 2.14 eV for Ba. In contrast, ordinary metals have work functions such as, for example, 5.6 eV for Pt, 5.1 eV for Au, 4.5 eV for Hg, and 4.3 eV for Ti. As so compared, alkaline, alkaline earth and lanthanum metals have a work function that is considerably lower than those of ordinary metals.

[0013] An alkaline, alkaline earth or lanthanum metal, which on the other hand is normally active, therefore has never been used, as a material to form a Schottky junction. However forming the same in an ultra high vacuum at a low temperature makes it usable as a material to form a Schottky junction.

[0014] Accordingly, as shown in Fig. 1, using silicon (Si) 1 as a semiconductor and sodium (Na) as an alkaline metal, we have formed a layer of Na in a thickness of 0 to 1 M. L. on the Si substrate to make up a Na/Si junction and measured the work function of the surface of the Si substrate. Results of measurement are graphically shown in Fig. 4.

[0015] To form this Na/Si junction, the surface of a Si substrate having a cleaved 7x7 pattern observable by RHEED is irradiated with Na metal in an ultra high vacuum by the MBE process. And, the irradiation at a K-cell temperature of 720°C makes it possible to form a Na layer of 1 M. L. in a time period of 10 minutes. In the graph of Fig. 4, the work function (W. F.) is plotted with respect to every incremental Na growth of about 0.1 M. L.

[0016] As is apparent from this graph, a decrease of about 2 eV in work function is found until the layer grows to 0.2 M. L. in thickness, and no much decrease is found if the layer is caused to grow more than 0.5 M. L. It is thus seen that a junction having a low work function metal of

about 1 M. L. applied on a semiconductor can be formed having a barrier ( $\phi_B$ ) that is a negative value. This can be used to form a junction of a semiconductor and a superconductor having a barrier that is low in height. To wit, as shown in Fig. 2 a superconductor 3 may be formed over a semiconductor 1 with the intermediary of a metallic layer 2 of an alkaline metal, an alkaline earth metal or a lanthanum metal, which has a low work function.

[0017] However, such a low work function metal is apt to be ionized and in general prone to diffuse into a solid body. For example, when use is made of Nb for the superconductor, therefore, a junction of Si as the semiconductor - Na as the alkaline metal with 1 M. L. - Nb as the superconductor is made, it has been common to make a layer of Nb by ion beam vapor deposition on the substrate that is heated at a temperature of 400°C. At such an elevated temperature, however, Na does come to diffuse away into both Si and Nb, thus permitting a Si and Nb junction to be formed and impeding the formation of a semiconductor and superconductor junction having a barrier that is low in height.

[0018] However, to prevent such diffusion, in making, for example, a junction of Si the semiconductor - Na the alkaline metal (1M. L.) - Nb the superconductor, limiting the temperature of the substrate when Nb is formed thereon to 0 to 150, for example, in a MBE apparatus of  $1 \times 10^{-10}$  Torr, at a EB rate of 1 Å/second and for a period of 100 seconds proved to make it possible for the junction to be successfully formed that is without a barrier and that is thus small in rectifying function.

[0019] For metals of a low work function other than those mentioned above, use may be made of K, Rb or Cs as the alkaline metal, of Mg, Ca or Ba as the alkaline earth metal, and of La, Pr, Nd or Sm as the lanthanum metal. Table 1 shows conditions under which each of these metals can be formed on a semiconductor to have a thickness of 1 M. L.

[0020]

[Table 1]

	Alkaline Metal				Alkaline Earth Metal			Lanthanum Metal			
K-cell (°C)	Na	K	Rb	Cs	Mg	Ca	Ba	La	Pr	Nd	Sm
	720	780	820	830	700	730	800	-			
E-gan	-	-	-	-	-	-	-	Formed with an Intensity of 0.1 Å/sec. and for a period of 30 to 60 seconds			

[0021] Table 2 shows metallic super conductors that can be formed in a layer on such a low work function metal and condition under which they can be formed.

[0022]

[Table 2]

	Nb	Nb/Au	Pb	Pb/Au	Pb/Ag/Au
E gun (Å/ sec.)	1	1/1	5	5/1	1/1/1
Thickness (Å)	1000	1000/300	1000	1000/300-500	1000/300/300
Sec.		1000/300		200/300	1000/300/300
Substrate Temp. (°C)	0-150	200-0/0-100	0-100	200-0/0-100	200-0/0-100/0-100

[0023] Next, referring to Fig. 5, mention is made of an example of this invention applied to a low energy type superconducting base transistor using an oxide superconductor.

[0024] In this example, use is made of a BKBO for the oxide superconductor. First, a  $\text{SrTiO}_3$  single crystal substrate 5 that is doped with Nb in an amount of 0.05 to 0.5 % by weight is prepared. And, this  $\text{SrTiO}_3$  single crystal



substrate 5 is washed using trichloroethylene, acetone and methanol. Washing is carried out by subjecting the substrate to ultrasonic waves in trichloroethylene for a period of 10 minutes, those in acetone for a period of 10 minutes and those in methanol for a period of 10 minutes. Subsequently to washing completed, the substrate is dried at a temperature of 120°C in a vacuum oven for a period of 10 minutes and thereafter is set in a vacuum chamber of a MBE apparatus. After an ultra vacuum of  $1 \times 10^{-10}$  Torr is established in this chamber, the SrTiO<sub>3</sub> single crystal substrate 5 has thermal cleaning applied thereto at a temperature of 720 °C for a period of 5 minutes.

[0025] Then, a film 6 of alkaline metal made of K or Rb with a thickness of 1 to 10 M. L. is formed on the SrTiO<sub>3</sub> single crystal substrate 5 set at a temperature of 300°C.

[0026] While this alkaline metal film is being formed, Bi and Ba cells are heated, too. After the alkaline metal film of K or Rb has grown to the thickness of 1 to 10 M. L., a Ba flux injection is commenced and an O<sub>2</sub> plasma is then introduced. Then, after all the cells are opened, a BKBO film 7 is formed on the alkaline metal film 6 to a thickness of 1000 Å.

[0027] The formed BKBO film 7 then by being exposed to a dry atmosphere has a natural barrier 8 formed thereon. This natural barrier 4 serves as a dielectric film.

[0028] Subsequently, the substrate 5 having the BKBO film formed thereon is introduced into a vacuum chamber of an electron beam vapor deposition apparatus to form on the natural barrier 8 an emitter region 9 made of Au with a film thickness of 1000 Å by electron beam vapor deposition. As a result, it is made possible to obtain a low energy type superconducting base transistor formed with a junction having practically no base and collector barrier ( $\phi_B$ ).

[0029]

[Effects of the Invention]

As set forth in the foregoing description, this invention makes it possible to lower the work function above a semiconductor and upon making thereon a junction with a superconductor makes it possible to form a barrier ( $\phi_B$ ) that is reduced in height, thereby raising the transmittance of quasiparticles therethrough.

[Brief Description of the Drawings]

[Fig. 1] It is a cross sectional view showing an example of this invention.

[Fig. 2] It is a cross sectional view showing an example of this invention.

[Fig. 3] Fig. 3(a) is a diagram of the energy band structure of a semiconductor; Fig. 3(b) is a diagram of the energy band structure of a superconductor; and Fig. 3(c) is a diagram of the energy band structure of a semiconductor and superconductor junction.

[Fig. 4] It is a graphical representation showing a relationship between the film thickness of a Na metal layer and the work function of the surface of silicone.

[Fig. 5] It is a cross sectional view showing an embodiment of this invention that is applied to a low energy type superconducting base transistor using an oxide superconductor.

[Fig. 6] It is a cross sectional view showing a conventional low energy type superconducting base transistor.

[Description of Reference Characters]

- 1 A semiconductor
- 2 A metallic layer (Na) having a low work function
- 3 A superconductor layer

る。そして、この $\text{SrTiO}_3$ 単結晶基板5をトリクレン、アセトン、メタノールを使って洗浄する。洗浄はトリクレン中に超音波10分間、アセトン中に超音波10分間、メタノール中に超音波10分間漬けそれぞれ行う。その洗浄が終わった後、真空オーブン120℃中で10分間乾燥させた後、MBE装置の真空チャンバー内にセットする。このチャンバー内を $1 \times 10^{-10}$  Torrの超高真空中に設定した後、 $\text{SrTiO}_3$ 単結晶基板5を720℃の温度による熱クリーニングを5分間施す。

【0025】そして、基板温度を300℃に設定し、 $\text{SrTiO}_3$ 単結晶基板5上にアルカリ金属のK又はRbを1~10M・L形成して、アルカリ金属膜6を設ける。

【0026】このアルカリ金属膜6の形成時に、Ba、Biのセルも加熱しておく。K又はRbのアルカリ金属膜6が所定の1~10M・L形成された後、Baのフラックス射出を始め、そして $\text{O}_2$ プラズマを導入する。その後全セルを開いてBKBO膜7をアルカリ金属膜6の上に1000Å積層形成する。

【0027】BKBO膜7の形成後後、乾燥大気にさらすことにより、BKBO膜3上に自然バリア8が形成される。この自然バリア4を絶縁膜として用いる。

【0028】次に、BKBO薄膜7が形成された基板5を電子ビーム蒸着装置の真空チャンバー内に入れ、Auからなる膜厚1000Åのエミッタ領域9を電子ビーム蒸着により自然バリア8上に形成して、ベース/コレク

タのバリア( $\phi_B$ )がほとんどない接合が形成された低エネルギー型超電導ベーストランジスタを得ることが出来る。

【0029】

【発明の効果】以上説明したように、この発明によれば、半導体上の仕事関数を低くすることができるので、この上に超電導体との接合を形成するとバリア( $\phi_B$ )の高さを低くすることが可能となり、準粒子の透過率を向上させることができる。

10 【図面の簡単な説明】

【図1】この発明の一実施例を示す断面図である。

【図2】この発明の一実施例を示す断面図である。

【図3】図3(a)は半導体のエネルギーバンド図、図3(b)は超電導体のエネルギーバンド図、図3(c)は半導体/超電導体接合のエネルギーバンド図である。

【図4】Na金属層との膜厚とシリコン上の仕事関数との関係を示す図である。

【図5】この発明を酸化物超電体を用いた低エネルギー型超電導ベーストランジスタに適用した実施例を示す断面図である。

【図6】従来の低エネルギー型超電導ベーストランジスタを示す断面図である。

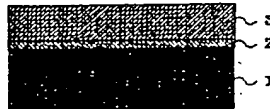
【符号の説明】

- 1 半導体
- 2 低仕事関数の金属層(Na)
- 3 超電導体層

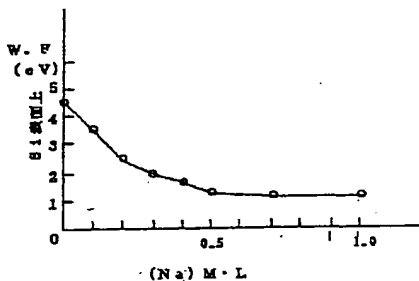
【図1】



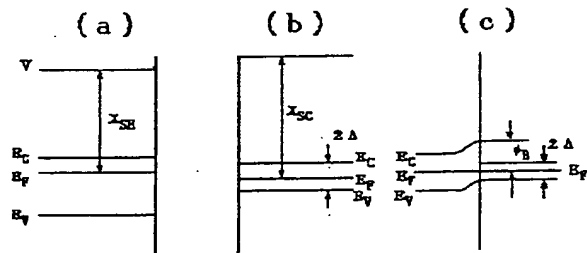
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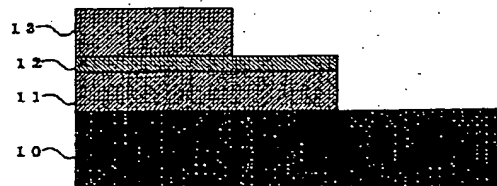
【図4】



【図3】

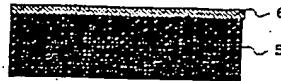


【図6】

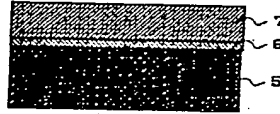


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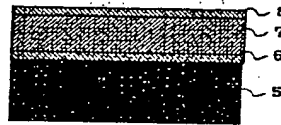
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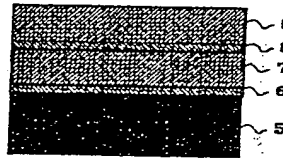
(b)



(c)



(d)



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